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SOLID-STATE HYDROGEN STORAGE MATERIALS OF APPLICATION
TO ENERGY NEEDS

Charles E. Lundin, et al

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SECOND SEMI-ANNUAL TECHNICAL REPORT

SOLID-STATE HYDROGEN STORAGE
MATERIALS OF APPLICATION TO ENERGY NEEDS

31 July 1975



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yields a second-order rate constant of 0.077 per second per unit ratio of H atoms to LaNi₅. Over the temperature range 15 to 25 degrees C., the activation energy is 21.9 kcal/mole. 3. Poisoning of LaNi₅ by air, oxygen and water was studied up to 100 degrees C with the conclusion that effects on hydriding are only temporary and limited to rate effects. 4. Preliminary hydrogen absorption-desorption measurements were made with 10 alloys and intermetallic compounds. These were selected compositions in the V-Cr and Nb-Mo systems, aluminum-saturated alpha-titanium, and the compounds CoTi, CeAl, CeAl₂, CeAl₄, and CeFe₅. A few of the results encourage further study.

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MATERIALS OF APPLICATION TO ENERGY NEEDS

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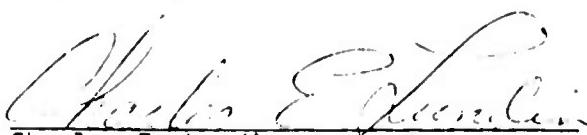
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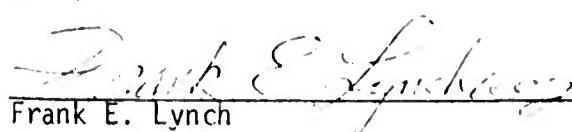
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I. TECHNICAL REPORT SUMMARY

During this six-months of report period, four general areas of effort were pursued. These were: 1) design and construction of an ultra-high-pressure hydriding apparatus, 2) completion of the hydriding kinetics of LaNi₅, 3) poisoning effect studies on LaNi₅, and 4) exploratory studies of potential new hydride systems.

The ultra-high-pressure hydriding system is being built to study the hydriding characteristics of alloys and compounds at much higher pressures than can be achieved in the existing systems which have been employed on this program. The current systems were designed to hydride at pressures up to 2000 psi, whereas the new system is capable of achieving 30,000 psi hydrogen pressure. The purpose of the new system is to have the ability to study pressure-temperature-composition relationship of unstable hydrides at least at an order of magnitude higher pressures. This pressure regime is of interest for two reasons. First, the search for higher absorptivity of hydrogen in current or new unstable hydrides is to be sought. Second, certain alloys or compounds may not activate until these pressures are attained due to tenacious surface contamination.

A major effort was conducted to obtain accurate data for kinetics of desorption of hydrogen from hydrided LaNi₅. This involved a series of designs of the kinetics reactor and subsequent desorptivity runs to evaluate each design. The evolution of reactor designs resulted in final optimized experiments to obtain the data which is presented in this report. First cycle desorption data at 25°C yielded an excellent fit to second order reaction kinetics with a rate constant of $7.7 \times 10^{-2} \text{ sec}^{-1} (\text{H/LaNi}_5)^{-1}$. Data were also taken as a function of temperature over a range of from 15 to 25°C. The Arrhenius plot of the data was constructed. The energy of activation was determined to be 21.9 Kcal/mole.

A study of the effects of surface contamination was made in LaNi₅ hydride. Two approaches were involved; 1) to evaluate the residual surface contamination on LaNi₅ in various experiments employing the kinetics of desorption, and 2) to intentionally contaminate LaNi₅ hydride with air, oxygen, and moisture at room temperature and elevated temperatures, then determine the difficulties in activation and the degree of total saturation of hydrogen in LaNi₅ at room temperature. The observations made as a result of these studies were several. First, the kinetics of desorption from surfaces that were made as fresh and clean as possible were found to be extremely sensitive to minor amounts of contamination. However, the resulting kinetics of desorption were still very rapid. From this scale of contamination to that of gross exposure to contaminants of air, oxygen, and moisture, the kinetics of reaction remained relatively high. Under severe conditions of exposure to air and pure oxygen at elevated temperatures, the activation, reactivity, and degree of saturation absorptivity remained surprisingly good.

During this report period the initiation of the enhancement studies was undertaken. Alloys were prepared in the arc furnace to the desired

stoichiometry and were prepared nominally for absorptivity evaluation by crushing to -100 mesh and loading into the reaction chamber. The intent in this phase of the program is to screen through as many alloys as possible. This will allow the identification of those materials which will hydride in an unstable mode similar to LaNi_5 and FeTi . The experiments are not designed to fully establish the pressure-temperature-composition relationship but to obtain the salient features. The features sought are a cursory isotherm at a convenient pressure-temperature level, a qualitative measure of kinetics of reaction under those conditions, a cursory vant Hoff relationship at three temperatures, the total hydrogen saturation at the selected isotherm, and the relative ease of activation. Later those alloys or compounds which exhibit promise can be evaluated in a fully quantitative manner. The alloys investigated so far include the following: selected alloys in the V-Cr system, selected alloys in the Nb-Mo system, CeAl_4 , CeAl_2 , CeAl , CoTi , CeFe_5 , and α solid solution saturated with Al. Several of these were activated and absorbed hydrogen in an unstable mode. Selected plots of isotherms are presented.

II. INTRODUCTION

This Semi-Annual Technical Report is the second of such reports due under Contract No. F44620-74-C-0020, Air Force Office of Scientific Research, and sponsored by the Advanced Research Projects Agency, Department of Defense under ARPA Order No. 2552-1. The report period is from 1 January 1975 to 1 July 1975.

The eventual application of hydrogen as an all-purpose fuel to phase in as fossil fuel supplies deplete is a distinct technological possibility. The embodiment of such a concept is exhibited by the growing advocacy of the "Hydrogen Economy" by many segments of the energy related industry. The most significant benefit is the clean, non-polluting mode of combustion, namely water. The environmental impact of its use compared to burning fossil fuels amounts to a near total solution to the World's current pollution problems. The combustion of hydrogen and air releases about three times as much energy per unit of weight compared to that of gasoline. Current limitations in the use of hydrogen are its cost, availability, an economical energy source to dissociate water, and the storage and handling. The first three factors will diminish as fossil fuels use decreases and nuclear-energy produced hydrogen increases to the point where hydrogen will be a viable fuel. The storage and handling problems are limitations which are serious, but certainly subject to modification. The hazards of shipping and handling of pressurized hydrogen in steel tanks are obvious and severe. The alternate storage of liquid hydrogen in cryogenic containers is also prohibitive because of the large investment in refrigerative cooling and cryogenic dewars. The solution to the storage and handling problems is one of the significant incentives in the research program addressed in this report. The approach is to use metallic hydrides as the means to contain the hydrogen gas. Materials such as LaNi₅ have provided a breakthrough in this respect. The development of this and more enhanced solid hydride materials would greatly accelerate the use of the hydrogen in energy applications.

The phenomenon of hydrogen absorptivity in LaNi₅-type compounds was discovered by scientists at Philips in Eindhoven, Netherlands. In studies of the effect of hydrogen on the permanent magnetic properties of these compounds, it was found by H. Zijlstra and F. F. Westerdorp [1] that SmCo₅ would absorb 2.5 moles of hydrogen at a pressure of 20 atm at room temperature. By removing the pressure, the absorbed hydrogen was released. Further studies by van Vucht, et. al. [2], extended this original work. They studied LaNi₅, SmCo₅, CeNi₅, and alloys of (La_{1-x}Ce_x)Ni₅ and verified the phenomenon. Both LaNi₅ and (La-Ce)Ni₅ alloys were found to absorb up to 6.7 and 7 hydrogen atoms per formula weight, respectively. The most important property of these compounds was their ability to absorb and desorb the large amount of hydrogen at room temperature and relatively low pressures (2.5 atm for LaNi₅). In each case the reaction was always initiated by a threshold pressure usually considerably higher than the equilibrium pressure of the isotherm. A gross lattice expansion and structural change accompanies the absorption. In LaNi₅ there is a 25% increase in the volume.

This is accompanied by severe stresses which fracture the initially solid compound. This factor can provide an extremely important side benefit. The new fresh surface and the increased surface area greatly speed up the kinetics of absorption and desorption. A loading-deloaded cycle of 10 times resulted in a fine powder with a subsequently constant active surface. Desorption rates were observed over a range of temperatures. At 25°C, about 100% of the hydrogen was removed against 1 atm of pressure in approximately 15 min. At 49°C, 100% of the hydrogen was removed in 5 min. The fully loaded LaNi₅ at room temperature and 2.5 atmospheres of pressure has a concentration of hydrogen atoms of 7.6×10^{22} atoms/cm³. This is nearly twice the density of liquid hydrogen. Furthermore, the desorption process allows only ultra-pure hydrogen to be released which is significant if only to provide an ultra-high purification process.

Further recent studies on LaNi₅ type hydrides [3-7] have still only cursorily delineated their properties and also their limitations as far as application. From additional studies on other hydrides of this same type, such as Mg₂Cu, Mg₂Ni, and FeTi [8-15], one can see emerging a whole new class of metallic hydrides. Hydrides have generally been known and thoroughly studied for many decades, but of a different class; that is, they have been what one might term, stable hydrides. They are metal-hydrogen systems that have high heats of formation, that do not decompose unless heated to high temperature, and that have extremely low dissociation pressures at room temperature. Many of the elements of the periodic table form these hydrides; the alkali metals, the alkaline-earth metals, the lanthanide series of metals, the actinide series of metals, and Group III, IV, and V transition metals. On the other hand, the new class of "unstable" hydrides have low heats of formation, have very high equilibrium pressures (several atmospheres) near ambient temperatures, and rapidly absorb and desorb large quantities of hydrogen with only minor enthalpy transfer.

Generally, the program plan is to carry on a multiphase effort to investigate the potential and test the feasibility of employing metallic hydrides to store hydrogen which would later be desorbed as a fuel for power or energy use. The materials under study will primarily consist of binary and ternary metallic systems of both intermediate phases and alloys thereof. The concept of using such materials as an energy source will be explored in terms of several fundamental property characteristics. The characteristics of principal interest are:

1. Pressure-temperature-composition relationships.
2. Kinetics of absorption and desorption.
3. Surface poisoning effects.
4. Potential safety hazards.

A systematic investigation of the hydriding characteristics of various alloy combinations will be made to develop better criteria for the prediction of the occurrence and extent of hydrogen occlusion in hydrides

that may be classified as unstable alloy hydrides. It is intended that a better understanding of this class of hydrides will emerge.

The program approach was modified somewhat after the decision was made within the Department of Defense to drop energy-related research. The current contract period will terminate the program rather than carry it for a third year as was originally anticipated. On consultation and negotiation with Dr. Stan Ruby of the Advanced Research Projects Agency and Dr. Joseph Masi of the Air Force Office of Scientific Research, the modified program plan was approved. The objective was to concentrate the effort during the remainder of this contract period in an extensive screening study of carefully selected alloys and compounds felt to have potential as unstable hydrides. The screening study obliges that for each material that is found to activate and absorb in an unstable mode, a determination will be made of 1) hydrogen absorptivity, 2) an isotherm at a convenient pressure-temperature level, 3) a qualitative measure of the kinetics of reactivity, 4) a vant Hoff relationship, and 5) the relative ease of activation.

III. DESIGN AND CONSTRUCTION OF AN ULTRA-HIGH-PRESSURE HYDRIDING APPARATUS

The design and construction of an ultra-high-pressure hydriding apparatus was initiated during the latter half of the previous contract period. The construction is essentially complete at this writing. The need for investigation of the occlusive properties of alloys or compounds for hydrogen in a higher pressure regime was first evident in the studies of the alloy, 60 w/o V-40 w/o Cr. The standard Sievert's apparatus is designed for pressures of about 2000 psi. Employing this, it was found in the V-Cr alloy that the isotherm at room temperature evolved a slope at the upper pressure limit which did not indicate saturation. Thus, the alloy has the propensity to continue absorption to much higher pressures. The total absorptivity to saturation would be of theoretical interest and can only be evaluated with the ultra-high-pressure apparatus. Further justification for building an ultra-high-pressure apparatus can be offered by the ability to activate through stubborn surfaces which may not otherwise activate at the lower pressures. Also, the existence of higher hydride phases in this pressure regime is possible. The detection of high-pressure plateaus in the total isotherm would only be feasible with this apparatus.

A brief description of the apparatus follows. The design in general is prototypic of the standard, lower pressure Sievert's apparatus. The exception is that the components are capable of extending beyond 2000 psi to a maximum pressure of 30,000 psi. The material employed in the tubing, the fittings, the valves, the reaction chamber, and other components is 316 SS. The system consists of a reaction chamber for the hydriding, a pressure gage in the range of 0 to 10,000 psi, an expansion pressure gage capable of measuring pressures to 30,000 psi, a vacuum source, and a high-purity hydrogen gas source whose output will reach 30,000 psi. Valves are interposed at the appropriate places. All components were purchased from the High Pressure Equipment Company, Inc.

The reaction chamber is a tubular cylinder incorporating a metallic collar and gland seal. The capacity is 6 cc. Moderate heating to 400°C at pressure can be attained.

The high pressure valves are supplied with collar and gland seals. O-ring seats and stem seals are of Buna "N". The valves and tubing are selected at 1/4" nominal sizing.

A pressure gage in 316 SS of the Bourdon tube type is employed up to 10,000 psi. Higher pressure Bourdon tube gages were not available in 316 SS, but only in hydrogen embrittleable steels, so a device was designed to extend the measuring range from 10,000 psi to 30,000 psi. This device is a 4 ft long, 1/4" diameter tube of 316 SS, welded shut at one end and connected to the system through a valve at the other end. The expansion due to pressure in the closed tube is used as a measure of the pressure. Calibration will be conducted with the Bourdon tube gage up to 10,000 psi and the calibration extrapolated to 30,000 psi as a function of extension. The extension of the length of the tube is measured directly

at the free, closed end by means of a Starrett gage, graduated to 0.0001". The extrapolated calibration curve can also be verified by calculating the extension at various pressures with the elastic modulus of 316 SS and Hooke's Law.

The vacuum source is a standard Welch fore pump separated by a bleed-off valve and a high-pressure valve from the Sievert's system.

The high-purity gas source that is capable of generating 30,000 psi of pressure is a heated reactor containing Mischmetal-Ni₅ hydride. This makes a convenient system because 30,000 psi can be reached at moderate temperatures while providing a high-purity hydrogen supply for the contiguous reactor containing the sample to be hydrided.

For safety purposes the system has been contained in an explosion-proof enclosure consisting of a double layer of 4 in" diameter sandbags.

The employment of this apparatus is planned for the next six-month report period.

IV. STUDY OF THE HYDRIDING KINETICS OF LaNi₅

A. INTRODUCTION

The determination of the kinetics of hydrogen desorption from LaNi₅ hydride was an extensive, difficult process complicated by two fundamental material properties; the high reactivity at ambient temperatures and the endothermic heat of reaction required in the desorption of hydrogen. These two factors coupled together made the task of maintaining isothermal conditions for the measurement a very difficult problem. In turn, the design of an appropriate reactor to carry out these measurements entailed a series of modifications until an optimum design was attained. The reactor had to incorporate two features to compensate for the properties of the LaNi₅ hydride in desorption. First, the reactor material and its configuration must allow excellent heat transfer to help maintain isothermal conditions. Second, the flow of hydrogen was so fast that the gas dynamics had to be taken into account in the reaction chamber and the inter-connecting manifold, the calibrated receiver volume, and the Bourdon tube gage. Also, it was found that the kinetics of desorption were very sensitive to various factors including initial particle size, sample history, number of hydriding cycles, amount of trace contamination in the system, and the sample preparation prior to charging in the system.

B. EXPERIMENTAL RESULTS

Various experimental approaches were employed in the study of the kinetics of desorption of LaNi₅ hydride. Improvements in technique evolved as the experience in taking data progressed. The desorption reaction is endothermic in the amount of 7.6 kcal/mole of H₂. In order to approach isothermality, the cooling effect in the particles must be countered by heat transfer from their surroundings. In a desorption reaction at 25°C for instance, wherein two-thirds of the gas is removed from the sample in about 5 sec., sustaining absolutely constant temperature is impossible. However, if the drop in temperature can be greatly minimized, the effect upon the kinetic data will be small. Various geometries of reaction chambers were employed. The 3/8" i.d. cylindrical stainless steel reaction chamber in which 8 gr. of sample were used for equilibrium measurements was inadequate. A similar reactor was fabricated using heavily finned copper walls in place of the normal 316 SS material. This allowed the observation of the intrinsic heat transfer properties of the hydride with little interference from the vessel.

The reaction rates observed using this reactor were not greatly improved, showing the hydride itself to be a limiting thermal resistance. The design objectives then were to reduce the size of sample, to greatly reduce the conduction path, and to provide a high thermal conductivity, high heat capacity mass with as much of its surface exposed to the powdered sample as possible.

A long helical spiral of 1/8" o.d. copper tubing was tried, but

the limiting factor found here was the throttling effect of the 1 μ sintered stainless steel filter and the long path length of gas escape through the packed hydride powder. The final geometry chosen was a pancake-shaped copper reactor in which the stainless steel filter was greatly increased in diameter. A 0.010" layer of LaNi₅ granules were placed into a 3" dia. circular recess machined into a 1/2" x 4" circular copper plate. The filter was placed over the powder and a grooved 1/2" x 4" circular plate was bolted over the filter with a viton "O"-ring forming a helium leak-tight reaction chamber. A very noticeable increase in desorption rate resulted from this change in reactor geometry. The reactor is shown in Figure 1.

Decomposition kinetics were measured by desorbing a ~4 gm. sample of LaNi₅H_{0.7} into a ~1200 cc evacuated volume and monitoring pressure rise as a function of time. The analytical treatment of the data assumes that the backpressure which builds from zero to about nine psi in the calibrated volume is insufficient to impede the desorption reaction.

Having thus overcome thermal and fluid dynamic limits, a new limiting phenomenon was encountered. Although throughout this entire study the utmost of cleanliness in materials and procedure had been applied, there was an increasingly obvious difficulty with trace surface contamination in the hydride samples which caused scatter in the data and deterioration with time and number of reaction cycles.

After deriving no benefit from a liquid nitrogen cold trap in the vacuum line, and very little effect from baking out the system at 120°C for several days, attention was turned toward the hydrogen supply. The hydrogen obtained from the National Bureau of Standards at Boulder, Colorado is at least 99.999% pure. However, considerable improvement was realized by installing a hydride storage unit between the tank and the test apparatus.

The storage unit consists of about 2000 gms of FeTi hydride in a stainless steel tube which is wrapped with electrical heating tape. The unit is charged with N.B.S. hydrogen until equilibrated at room temperature then purged rapidly several times by venting through a high volume vacuum pump and allowing the pressure to build between each venting.

The only remaining possible source of contamination that could be discovered was the plastic seals used in the valves of the system (Teflon) and the O-rings in the reactor (Viton). The valve seals could not be altered without considerable revision of the apparatus. The viton O-rings were replaced with copper seals by modifying the reactor but the problem remained.

It is presently felt that only by constructing an apparatus with ultra-high vacuum technology, will it become possible to approach the

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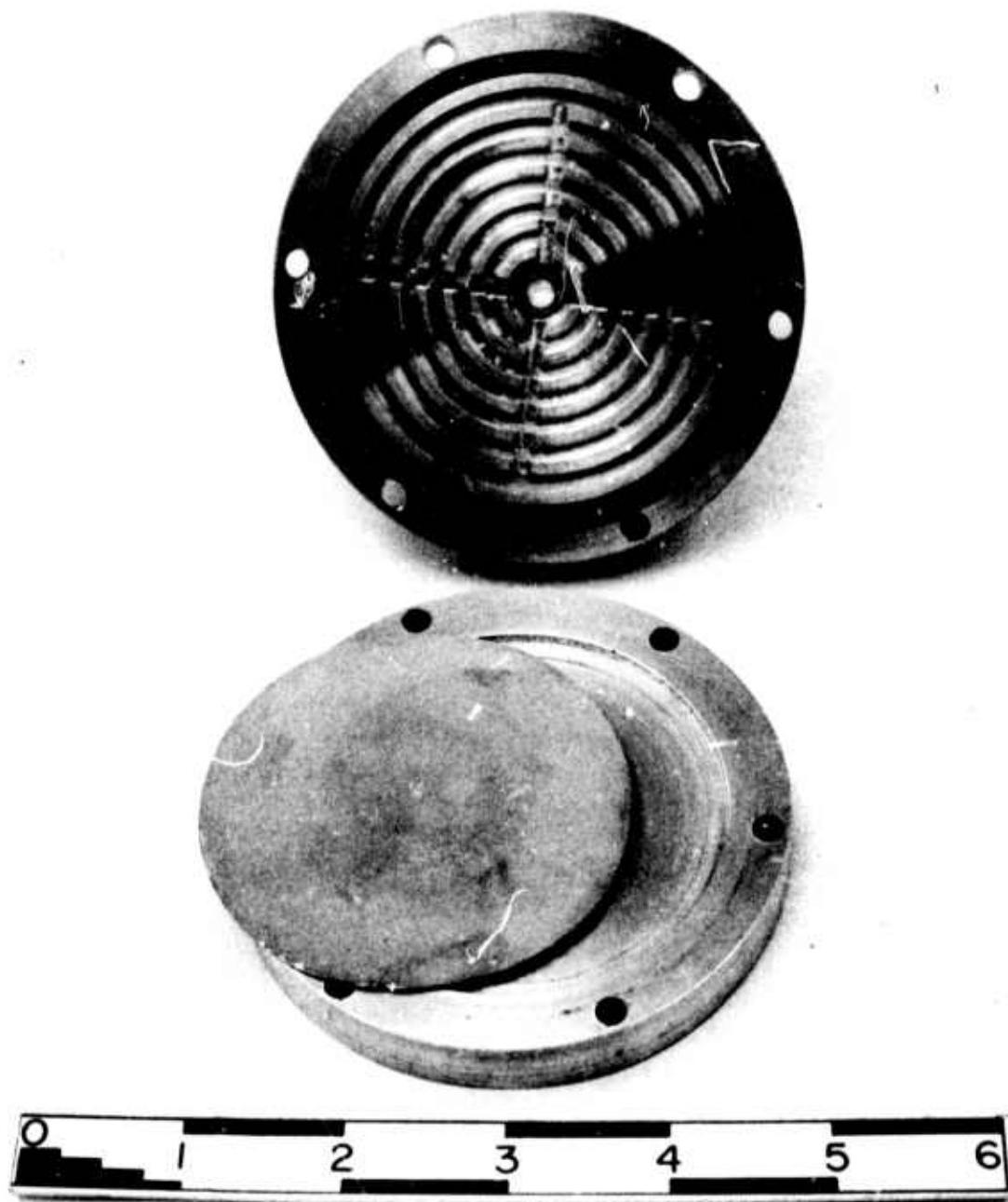


Figure 1. Internal View of the Copper Flat-Plate Kinetics Reactor and Filter Assembly.

absolute limit of reaction speed for LaNi₅ hydride decomposition.

The final kinetics of desorption data on LaNi₅ hydride were obtained with the flat plate reactor shown in Figure 1 and the careful vacuum processing approaches described above.

First cycle desorption data at 25°C yielded an excellent fit to second order reaction kinetics with the rate constant, $7.7 \times 10^{-2} \text{ sec.}^{-1}$ ($\text{H/LaNi}_5\text{)}^{-1}$. Data by Reilly and Wiswall¹⁶ were reported on the kinetics of decomposition of LaNi₅ hydride in a similar experimental approach. First order kinetics were found with a rate constant at 30°C of 0.10 sec^{-1} . This rate is considerably slower even at a higher temperature. With the geometry employed, the data would be suspect of larger deviations from isothermal conditions.

Although the data had considerable scatter for reasons described previously, an Arrhenius plot was prepared of $\ln k$ (reaction rate constant) versus reciprocal Absolute temperature. The data were taken in the temperature range from 15 to 25°C. The plot is shown in Figure 2. The activation energy determined from this plot is -21.9 Kcal.

Second, third and fourth desorption cycles showed a gradual deterioration of kinetics. Accumulating surface contamination was the suspected cause of this deterioration so the sample was exposed to 1 atm. of air at room temperature for 2 hours. The subsequent saturation and desorption reactions were extremely sluggish but the saturated composition was unaffected.

A series of 70 additional saturation-desorption cycles were performed, checking the kinetics at convenient intervals. A gradual recovery was noted which after two or three cycles yielded desorption rates adequate for most engineering purposes. By the seventieth post-exposure cycle the kinetics had fully recovered to the value observed on the fourth cycle, just before the air exposure.

Optical and electron microscopy methods were employed to determine if the cause of this recovery phenomenon was subsizing of the powder particles and hence the creation of fresh surfaces. No significant deviation from the particle size distribution at 10 and 20 cycles was found. The average particle size was determined to be 8 microns.

Although the amount of internal microfracturing of particles is impossible to assess, it seems likely that the recovery phenomenon results from the flushing of contaminants from the surface rather than from the creation of new surface.

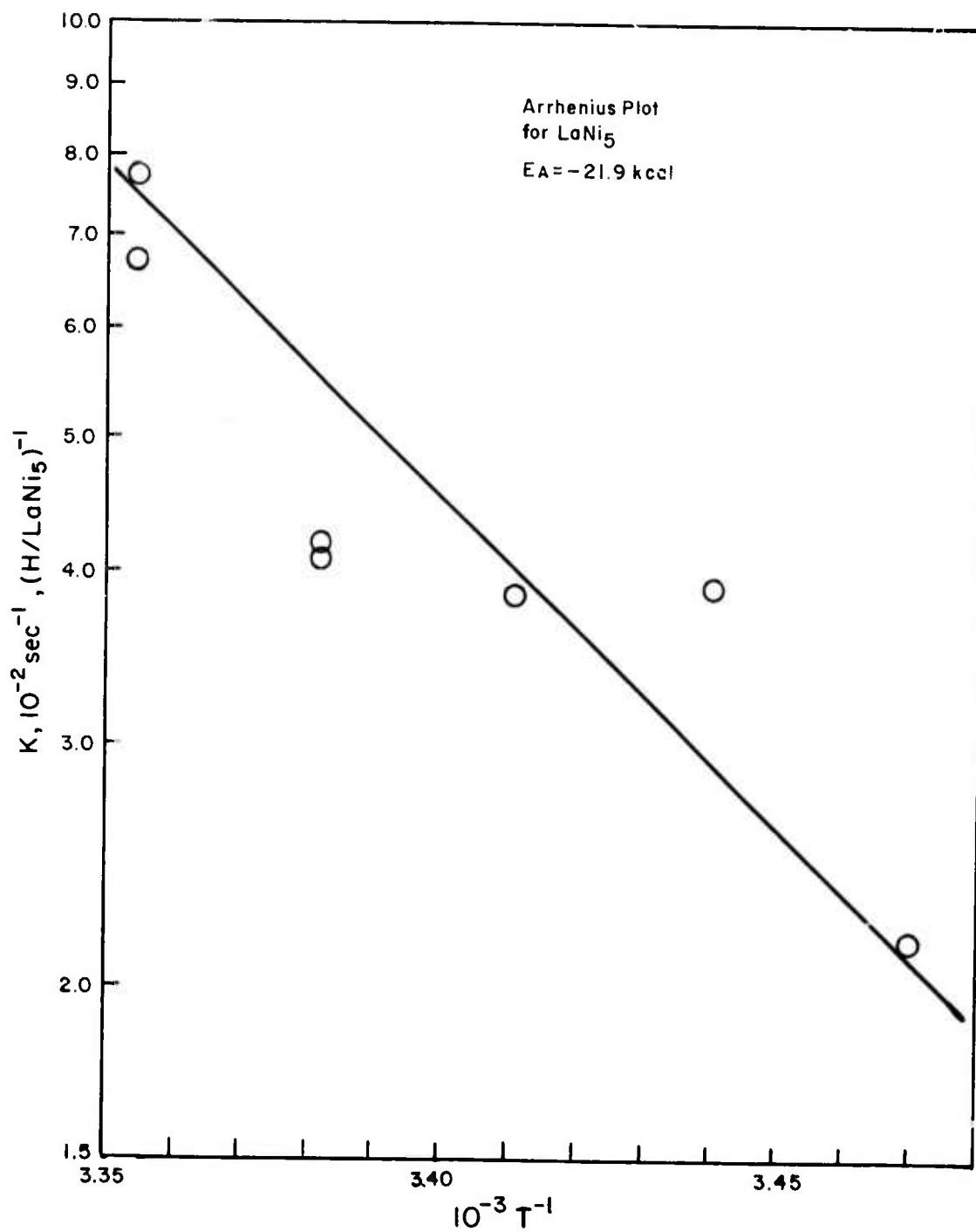


Figure 2. Arrhenius Plot for the Kinetics of Desorption of Hydrogen from LaNi₅ Hydride

V. POISONING RESISTANCE OF LaNi₅ HYDRIDE

During the collection of P-T-C and kinetics data, it became increasingly apparent that LaNi₅-hydride exhibited minor variations in its properties that were attributable to trace surface contamination.

Since the test apparatus was operated at purity levels which would be difficult to maintain in most practical systems, it is important to know the response of LaNi₅-hydride to gross contamination.

The series of curves in Figure 3 shows the gradual deterioration of hydrogen desorption kinetics as a function of cycles in curves "1" through "4". The curve labeled "5" was recorded after intentionally contaminating the sample with room air at 25°C and rehydriding. Curves "7" and "9" show the recovery process which, after ~75 cycles had restored the kinetics to about the same value as cycle "4".

It is noteworthy that the cleanest run, run #1, gives 2nd order kinetics with $K=3.6 \times 10^{-2}$, while post contamination runs #5, #7, and #9 yield 1st order data with K ranging between 2.6×10^{-3} and 8.0×10^{-3} . Runs #2, #3, and #4 do not conform to any integral order of reaction.

The susceptibility of LaNi₅ to poisoning by air, O₂, or H₂O at temperatures up to 100°C was found to be only temporary and limited to the kinetic behavior. The ultimate H/LaNi₅ saturation value was unaffected if sufficient time was allowed for equilibration.

Prolonged exposure to pure O₂ at temperatures above 300°C will completely oxidize the LaNi₅ preventing any further reaction with H₂, but if the sample is only partially burned the remainder will hydride showing that the oxide is permeable.

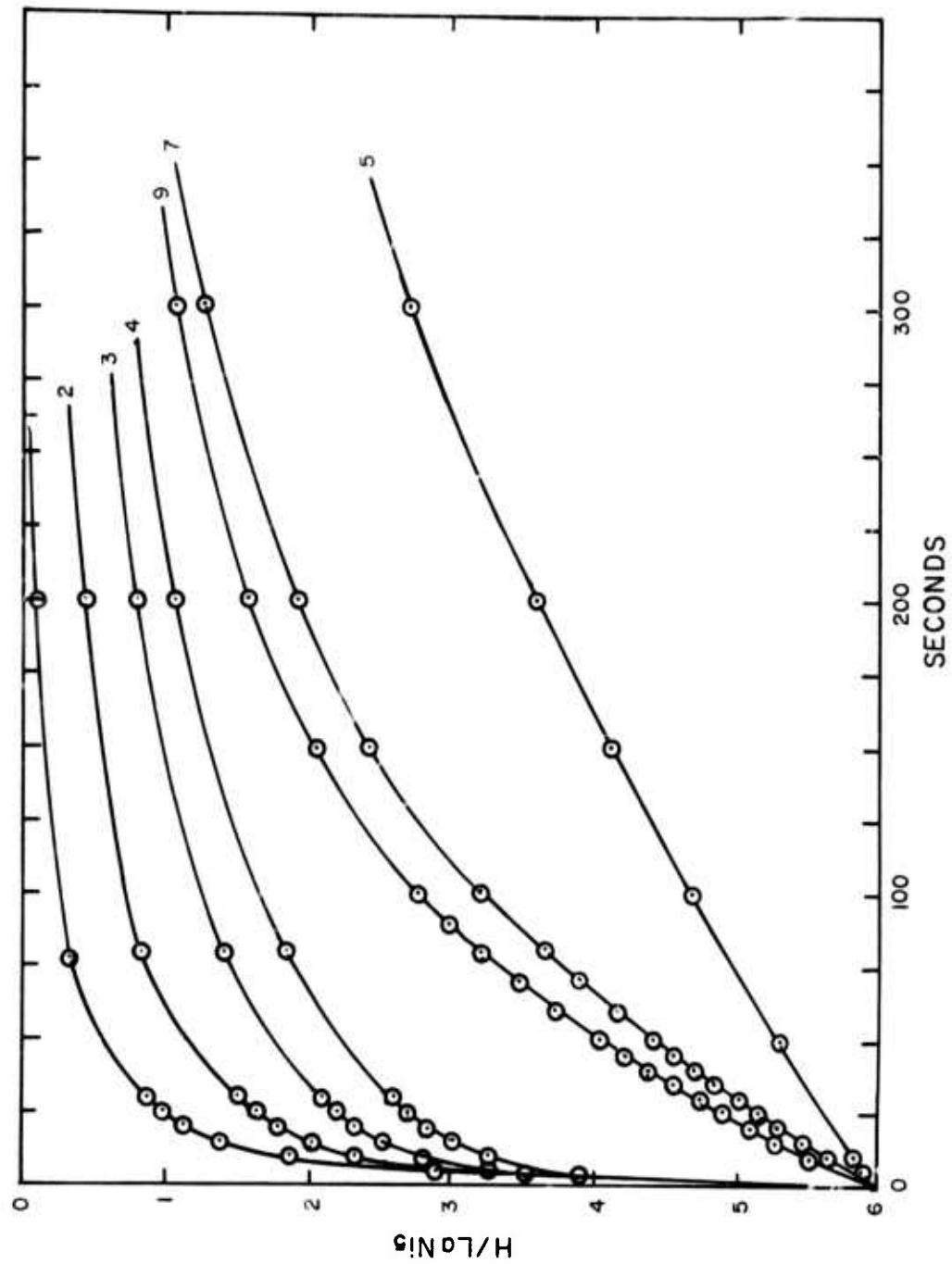


Figure 3. LaNi₅-H Desorption Kinetics Sample #7: runs 1,2,3,4,5,7,9. Air exposure between runs 4 & 5.

VI. EXPLORATORY STUDIES OF NEW HYDRIDE SYSTEMS

A. INTRODUCTION

Although some investigations were initiated in the last few months of the previous contract period, the exploratory and screening studies for new unstable hydrides were not fully undertaken until after the kinetics of hydrogen desorption from LaNi_5 were completed during the past several months. This phase of study is designed to search, select, and screen for alloys that appear to have promise as potential unstable hydrides. The ultimate goal of this program is to develop hydrides that demonstrate excellent storage and retrieval of hydrogen capabilities for subsequent power or energy application. Generally, the properties sought for an ideal storage material are as follows:

1. High saturation capacity for hydrogen
2. Reasonable density of metal or hydride
3. Low heat of reaction
4. Surface passivity to contaminants
5. Rapid kinetics of absorption
6. Near ambient pressure-temperature relationships
7. High thermal conductivity
8. Low heat capacity
9. Ability for indefinite recycling
10. Stable powder size after several cycles
11. Safe materials to handle and use
12. Low cost materials

Obviously, one cannot achieve all of these properties simultaneously in one hydride. However, an adequate compromise must be found compatible with the application resulting in a material that is suitable for efficient use, practical operation, and reasonable cost. It is felt that the experimental approach employed in this program will maximize the possibilities of finding hydrides with such criteria of suitability.

B. APPROACH

The approach taken in this phase was to select promising candidates of both binary and ternary systems based on what is currently known of hydrides, in general. Since the unstable hydrides are relatively recent in development, the current state of knowledge is very rudimentary. Thus, the criteria for selection from principle does not exist. Various guidelines were employed, however, which should greatly increase the probabilities of selecting and developing new hydride materials from binary and ternary metal compounds. The guidelines were as follows:

1. For intermetallic compounds, the selection of structure-types that are compatible with hydriding were chosen.

2. For ternary compositions, a rationale for selection was followed, such as the search for possible pseudo-binary systems for solid solutions of binary intermetallic compounds.

3. Considerations of the valence, the atomic diameter, electron concentration, size of interstices, and electronic structure were taken into account as one would with the stable hydrides.

4. A liberal use of transition metals in Groups III, IV, and V transition metals was sought because of their known propensity to hydrogen occlusion.

5. The avoidance of the surface-active elements because of the possible poisoning activity was stressed.

6. The selection of predominantly brittle materials was made, since microfracture is felt to be a criterion of optimum kinetics of desorption.

7. Attention was closely paid to the ternary and quaternary phase equilibria in the rationale of selection.

8. Selection was made of elements of the system which are reasonable in cost, although this was not always followed if some fundamental insights could be divulged.

9. The use of elements in the alloy systems with a density of less than about 8.5 grams/cc, was generally followed for the practicality of application.

10. Quaternary addition elements were selected in some cases for possible passivation of the surface to poisons.

11. The selection of intermetallic compounds with at least one of the multiple of elements capable of forming a hydride was followed.

C. EXPERIMENTAL

Alloys were prepared by arc melting the stoichiometrically prepared charges in an inert atmosphere of argon. The button homogeneity was assured by inverting the button and melting four times. Metallographic analysis was routinely conducted on the completed alloy buttons to assess the structural homogeneity. In all cases thus far, the melting procedure has proven to provide the appropriate starting material for hydriding.

In general, the procedure for preparation of the material for charging in the Sievert's reaction chamber has been to crush or to file the material to -100 mesh particles. This is done in an enclosed glove box with a purified helium atmosphere. The granular material is then weighed by removing the charge in a weighed and sealed glass vial

to a Mettler Balance. A charge of about 3 to 4 grams is usually prepared. After weighing, the vial is brought back within the glove box where it is loaded into a reaction chamber. A valve in the line above the reaction chamber allows enclosing the sample in a purified helium atmosphere. This assembly can be removed from the glove box and attached to the Sievert's apparatus. Evacuation of the reaction chamber can then be initiated. The sample is pumped to a partial pressure of several microns at which time flushing and evacuation with high-purity hydrogen is employed prior to the activation procedure.

The activation procedure adopted for unknown samples is generally as follows. After evacuation, high-purity hydrogen at 600 psi is imposed on the sample. Sufficient time is allowed at room temperature to determine whether absorption has been initiated. At least four hours is allowed to elapse in this stage. If absorption does not occur, the pressure is increased to between 1500 and 2000 psi. Again, time is allowed at room temperature for the incubation of absorption. Should this not be sufficient, the sample is heated to elevated temperature, nominally about 400°C. The pressure of hydrogen is maintained up to temperature. Usually, one observes absorption before 400°C is reached. This pressure and/or the temperature is maintained until full absorption has been achieved. The temperature stability is then checked out by lowering the chamber to room temperature. In order to completely break-in the sample to hydrogen occlusion, the sample is dehydrated and rehydrated several times at room temperature if the kinetics are fast enough. If not, the temperature is increased to some nominal value up to about 350°C until reasonably fast kinetics are observed.

An absorption or desorption cycle is then initiated to obtain an isotherm. Measured amounts of gas are either admitted or removed in incremental steps, each being allowed to attain equilibrium, to plot a pressure-composition relationship at the chosen temperature. The complete isotherm is produced in this manner from complete saturation to depletion of hydrogen. From the calibrated volume of the system, calculations of the incremental changes in composition are made.

The vant Hoff relationship is determined for those systems demonstrating reasonably flat plateaus. The vant Hoff plot is the pressure-temperature relationship at constant composition. Three temperature levels are selected and the pressure equilibria are determined. The vant Hoff equation of the general form,

$$\ln p = -\frac{A}{T} + B$$

is then evaluated. From the slope, A, a heat of reaction is obtained.

D. RESULTS

During this report period, a total of 10 different alloy specimens

were investigated. The alloy systems represented were; V-Cr, Nb-Mo, Ce-Al, Ti-Al, Co-Ti, and Ce-Fe. The V-Cr and the Nb-Mo systems are solid solutions throughout. The Ti-Al alloy selected was the α -Ti saturated solution of Al with ~35 a/o Al. Three compounds were evaluated in the Ce-Al system; CeAl, CeAl₂, and CeAl₄. One compound in the Co-Ti system was studied, the equiautomic composition at CoTi. This compound is isomorphous with FeTi. One compound in the Ce-Fe system was studied, CeFe₅. This compound is isomorphous with LaNi₅.

The V-Cr system was studied in the range of 40 w/o Cr to 70 w/o Cr. The 60V-40Cr alloy was evaluated first. Activation initiated readily at 25°C and 600 psi. After several cycles of absorption and desorption, a desorption run was initiated on a saturated sample. The desorption curve is presented in Figure 4. The scale of composition is relative, since all of the gas in the sample was not accurately determined because of the manner in which it was run. However, as can be seen, more than one atom of hydrogen per formula weight of alloy was removed. At about one atmosphere of hydrogen, the desorption run could no longer be continued, because of the lack of driving force in desorption. Thus, a total measure of the amount of gas was impossible. Since vanadium forms a monohydride in the subatmospheric region, it is felt that the desorption curve in Figure 4 is in the monohydride-dihydride region. A quantitative measure of total absorptivity is currently being checked by reproducing the isotherm in absorption.

A 30V-70Cr alloy at the other end of the composition range was evaluated. Very small uptake of gas was observed. A saturation value of hydrogen was not obtained because it was found to be insignificant. Thus, the absorption in the chromium-rich region of the V-Cr solid solution system is consistent with the fact that Cr by itself does not absorb in a hydrogen gas atmosphere. This system was of interest because Cr has been reported to form trihydrides under conditions of evolution of hydrogen by electrolysis. The V-Cr alloy system provided a means to evaluate the gradient in absorptivity in the solid solutions from the V-rich end, where an unstable hydride forms, to the Cr-rich end, where no data existed. However it is obvious from these data that the unstable hydride disappears as one approaches the Cr rich region, as does all absorptivity.

The Ce-Al system was studied in the form of three intermetallic compounds; CeAl, CeAl₂, and CeAl₄. The CeAl compound was found to activate readily at room temperature and 600 psi hydrogen pressure. The saturation of hydrogen in the compound was determined to be of the formula, CeAlH_{2.8}. The absorptivity was significant in quantity of hydrogen. However, the hydride was found to be very stable. The pressure equilibria were well under the ability of the Sievert's system to measure employing the Heise gauge. Thus, to remove the hydrogen, the sample had to be heated and fully pumped on with the fore pump. The CeAl compound is peritectic in formation. Attempts to activate the CeAl₂, a congruent melting compound, were negative. The CeAl₄ compound is also peritectic in its formation. Attempts to activate

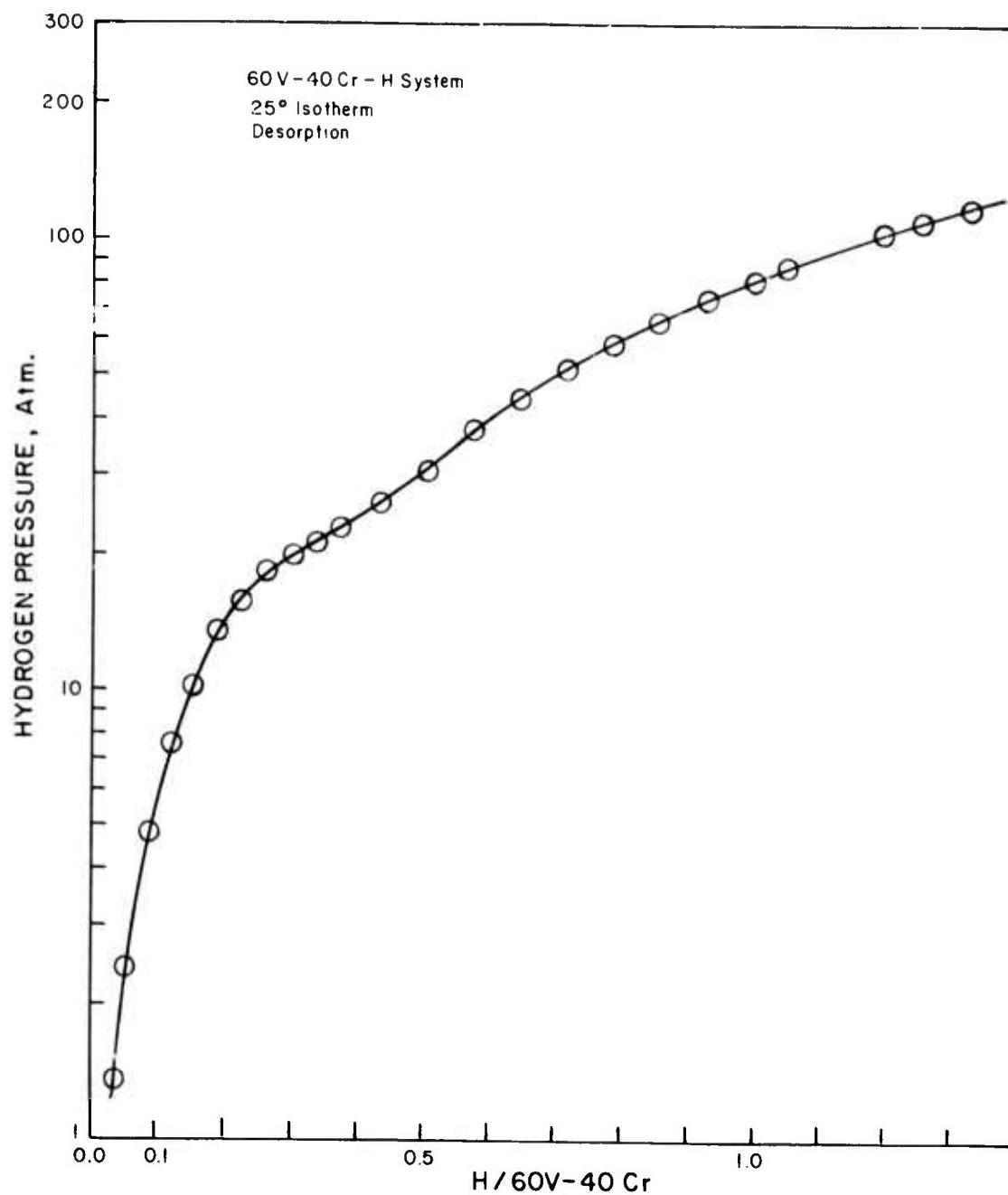


Figure 4. Plot of the 25°C. Isotherm of the 60V-40Cr Alloy

CeAl_4 were somewhat more responsive. A slight solubility of hydrogen was recorded, but not enough to get an accurate quantitative measure.

The Co-Ti system was studied next in the form of the compound CoTi . Activation was achieved at 25°C and 600 psi. The activation was slow, requiring several days to saturate. After several cycles an absorption isotherm was determined. A temperature of 100°C was employed to accelerate the kinetics. Figure 5 shows the isotherm. A saturation of about $\text{CoTiH}_{1.4}$ was obtained at about 35 atmospheres pressure. A plateau was observed at about 0.35 atmospheres.

The Ti-Al system was of interest because of the large solubility of Al in α -Ti. An alloy was prepared at 35 atomic percent of Al. Activation of this sample was achieved at 25°C and 1000 psi pressure. The kinetics of absorption at 25°C were moderate. After cycling several times, an absorption isotherm was obtained at 25°C . The plot is seen in Figure 6. Saturation absorption was obtained at $\text{Ti}_{.65}\text{Al}_{.35}\text{H}_{1.3}$ and 60 atmospheres. Although most of the dilute hydrogen region represents a stable hydride, the alloy is of interest because of the trend in the more saturated region toward an unstable condition. It is felt this alloy will provide a good base for quaternary alloy studies.

The Ce-Fe system was represented by the CeFe_5 compound which is of interest, because it is isomorphous with the LaNi_5 structure, D_{2d}. The sample activated rapidly at 600 psi and 25°C . Several cycles of absorption and desorption caused further breaking-in. The kinetics were extremely rapid thereafter. The saturation absorptivity was determined to be about CeFe_5H_4 at 600 psi and 25°C . A desorption isotherm at 100°C was then produced as can be seen in Figure 7. A plateau was observed at about .75 atmospheres. The vant Hoff relationships were obtained next at about a ratio of 1.0 H/ CeFe_5 . The plot is presented in Figure 8. The slope was treated from the vant Hoff plot to produce $\Delta H = -19.7$ Kcal/mole of H_2 for a heat of reaction. Investigators at Brookhaven [16] studied CeFe_5 and found an absorptivity similar to that in this investigation. Their value of total absorptivity was similar. No vant Hoff data were determined.

The Nb-Mo system is of interest for the same reasons as the V-Cr. That is, Nb metal forms an unstable hydride from 1.0 to 2.0 H/metal ratio. The Nb-Mo alloy system is a solid solution throughout. In an earlier study by one of the authors [17], the alloys in the 30 to 40 weight percent Mo were observed to fracture violently and then absorb hydrogen at room temperature. The current interest is to determine whether the Mo caused optimization of the formation of an unstable hydride in V. First, a 50Nb-50Mo alloy was subjected to activation. Various combinations of pressure and temperature did not cause any uptake of hydrogen whatsoever. Next a 70Nb-30Mo alloy was investigated. This study is currently still in progress. To date, it has been found that activation was achieved and absorption of considerable hydrogen has occurred.

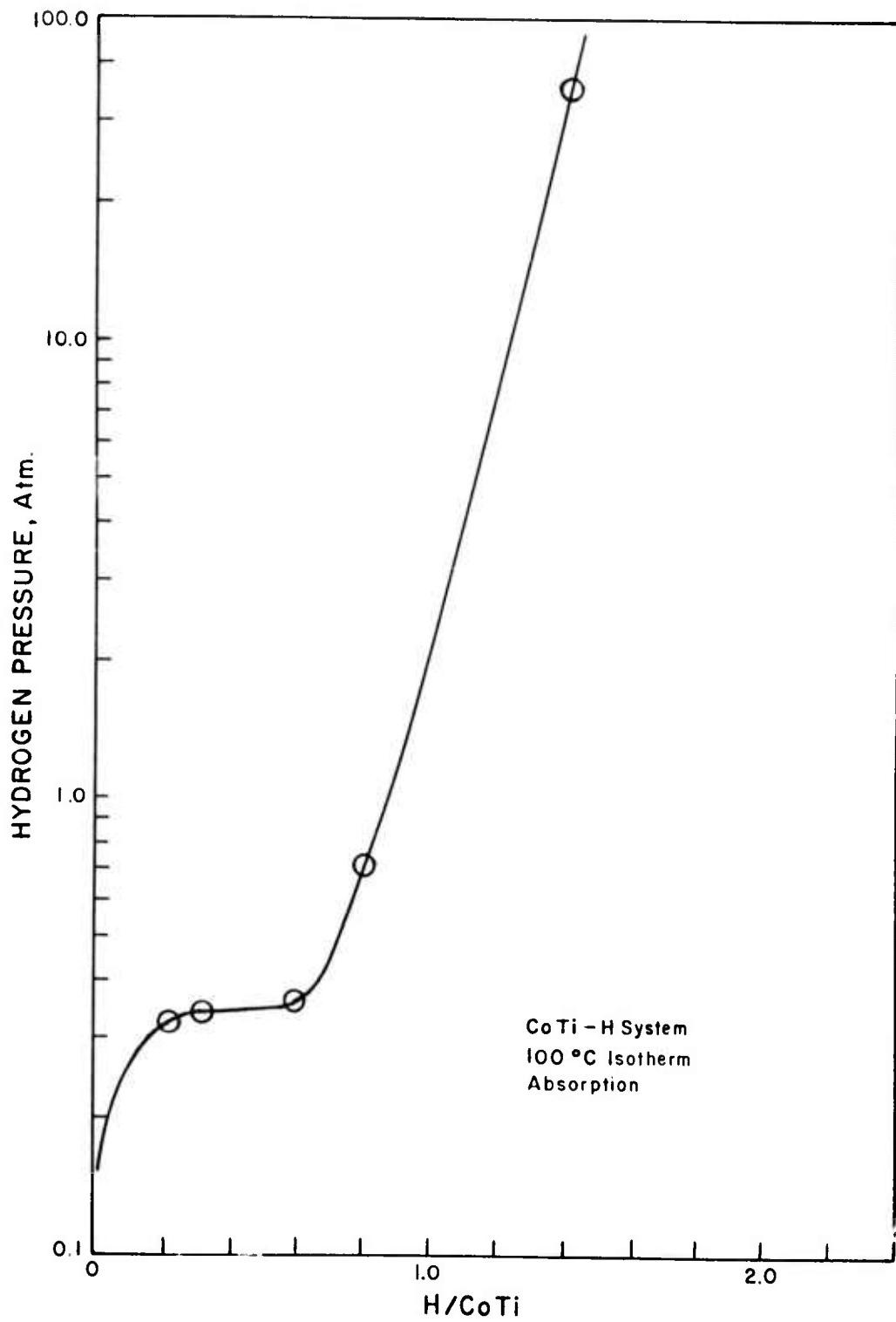


Figure 5. Plot of the 1000°C Isotherm of the CoTi-H System

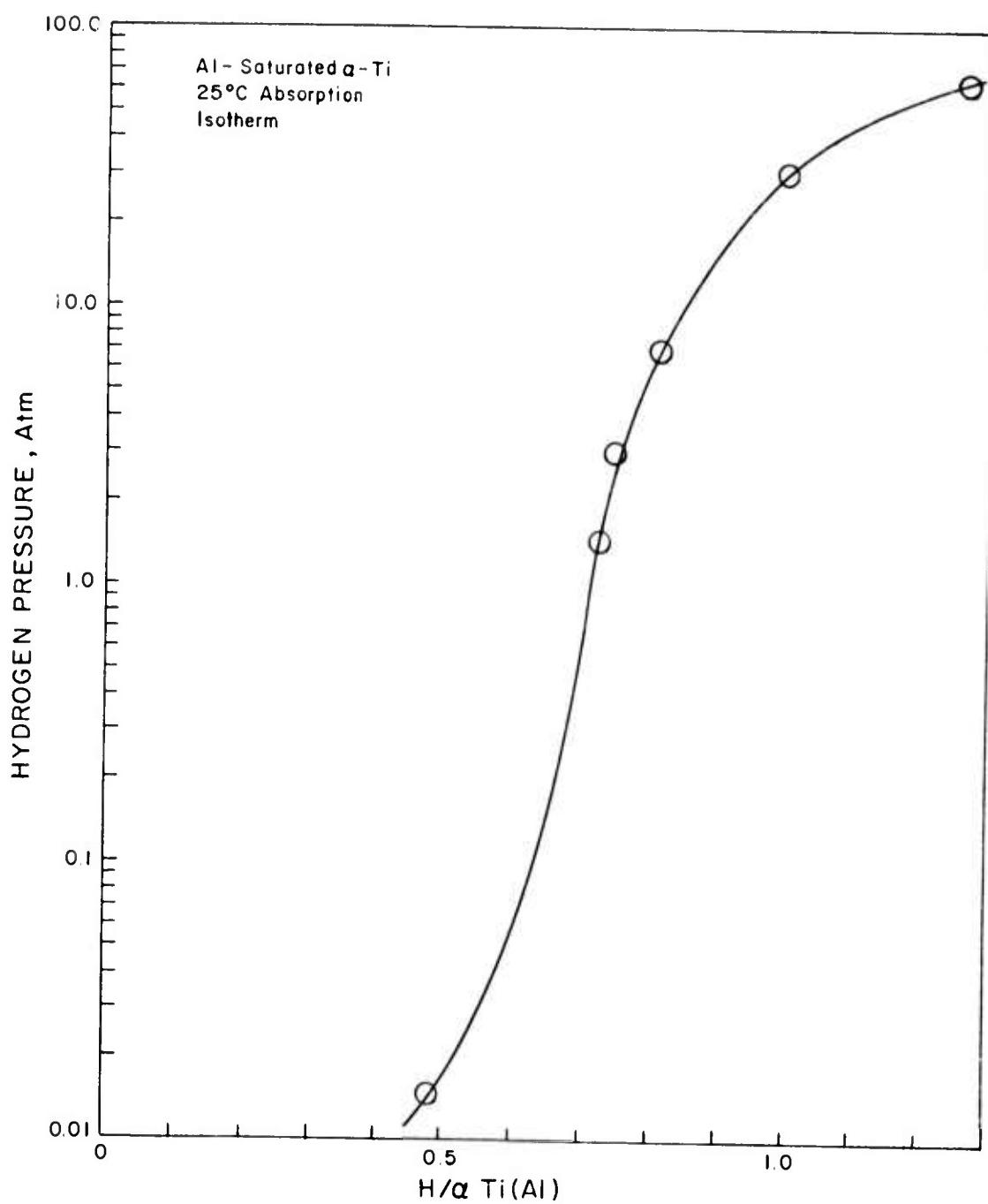


Figure 6. Plot of the 25°C Isotherm of the α Ti(Al)-H System

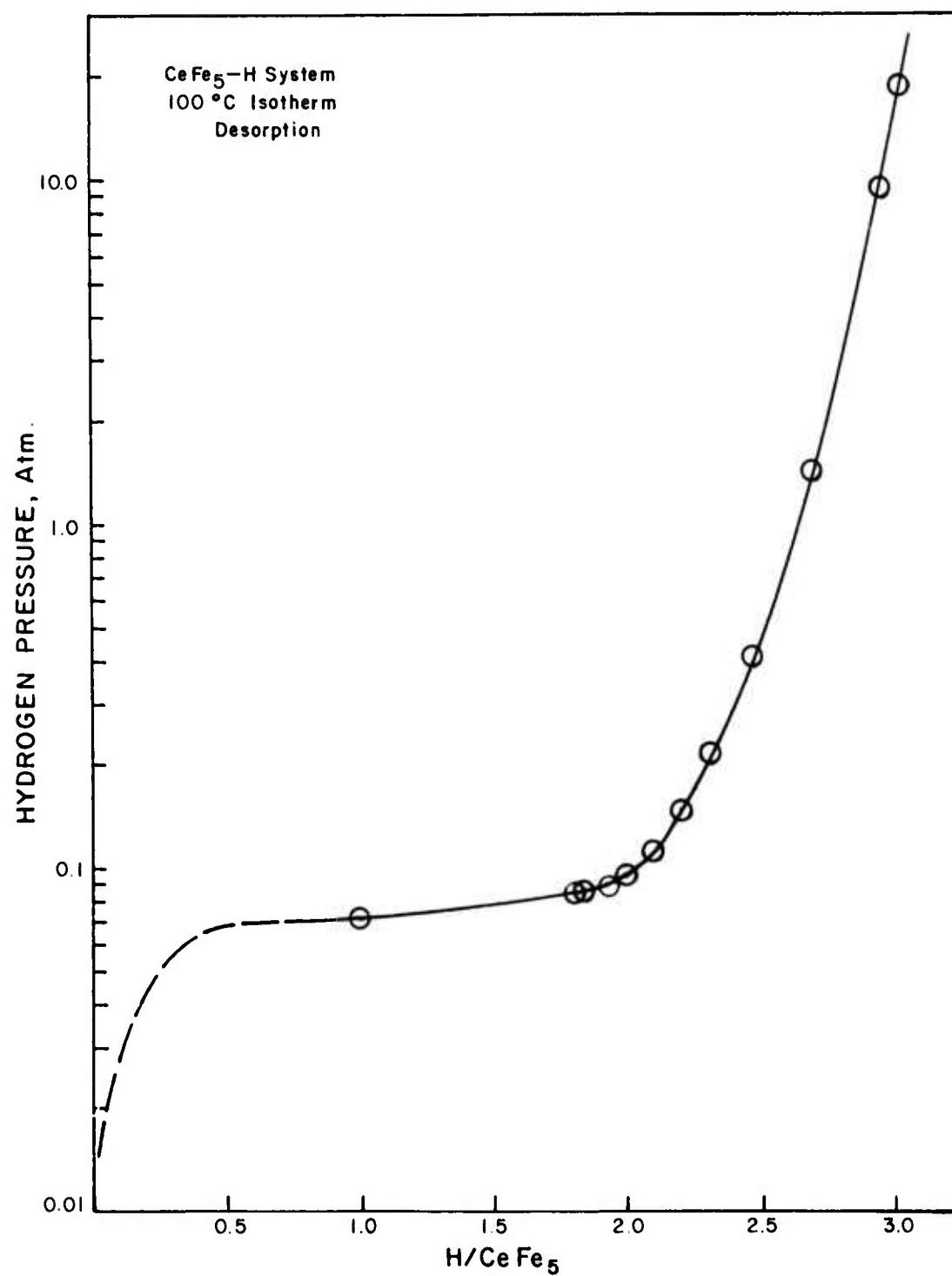


Figure 7. Plot of the 100°C. Isotherm of the CeFe₅-H System

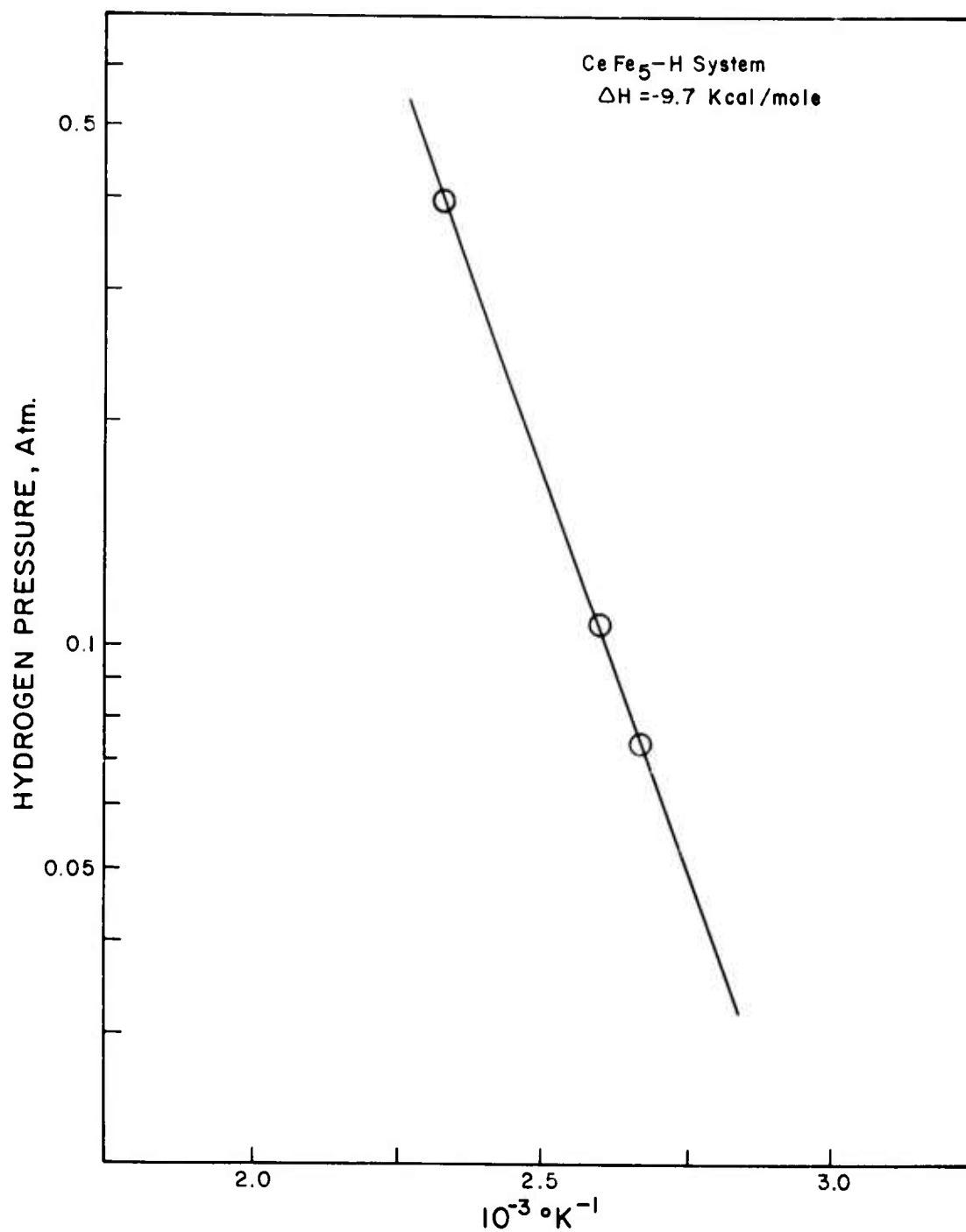


Figure 8. Van't Hoff Relationship for the CeFe₅-H System

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